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(54) Title: THE MANUFACTURE OF AND USES FOR LOW MOLECULAR WEIGHT AGARS AND AGAROIDS

(57) Abstract

The invention consists of methods by which agar or an agaroid is hydrolysed under controlled conditions to give materials which form very low strength gels when 1 % solutions in water are cooled, and which, at near zero gel strengths, give dispersions which act like creams. These can be used as bases for skin treatment products, cosmetics, food and have the advantage for skin preparations of being handled like a cream but then behaving like a lotion, the cream leaving no oily residue. Twelve examples are given, including uses for cosmetics, massage gels, etc., and twenty claims are made.

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DESCRIPTION OF INVENTION

THE MANUFACTURE OF AND USES FOR LOW MOLECULAR WEIGHT AGARS AND AGAROIDS.

This invention relates to methods of making agars with very low gel strengths, and the discovery of uses for these materials.

According to the US Pharmocopeia, agar is a hydrophilic colloid which can be extracted from certain seaweeds of **Rhodophyceae**. Its characteristic property is that it is insoluable in cold water, and if 1.5% parts by weight are dissolved in hot water, on cooling it forms a firm gel. Agar is generally considered to be a mixture of agarose and agaropectin, the agaropectin being a low (or even zero) gel strength colloid and consisting of an agarose type molecular backbone but with a high level of sulphate esters and of pyruvate ketal. Agaropectin itself is not, by itself, an item of commerce.

Agar is generally used industrially because of its rather unusual gelling properties, and the gel strength of an industrial agar of 1.5% concentration generally lies between 600-1100g/cm^2. Lower gel strength agars occur through traditional manufacture in Asia, and gel strengths of 450g/cm^2 are tolerated (Armisen, 1987) but are considered inferior.

There are, however, a number of seaweeds which give agar-type extracts with very low gel strengths, presumably because they have low molecular weights. These seaweeds are not extracted commercially, because there is no known use for their extracts. For the purpose of this disclosure, the term "low gel strength" refers to gels with a strength of less than 150g/cm^2 for a 1.5% gel, and ideally less than 40g/cm^2, when measured by the force needed to rupture a gel when applied through a plunger of surface area 1cm^2. A number of other agar bearing seaweeds give low gel strengths when extracted, but when treated with

alkali following methods known to those practised in the art, give an agar with a higher gel strength. These initial weak gels tend to rupture, and in the limit of weakness flow as a sloppy gel. These materials generally consist of agar molecules which have high levels of anionic substitution, for example, sulphate ester, and the preparation of such materials are not the subject of this invention, although their incorporation in agars for the uses outlined below, even if they are not desirable, is intended to be within the scope of this invention.

If, however, an agar without such anionic substitution can be made as a weak gel, rather than giving the sloppy gel noted above, it gives a solid which on agitation or stirring gives a rather unusual creamy texture and with unusual water retention properties. The best gels for some of the purposes of this invention are gels which have a low gel strength specifically because of the lower molecular weight, and paradoxically are best prepared from high gel strength agars.

There are already a number of thickeners and gels on the market which have a number of uses, particularly in the food industry, and the uses are generally based on water retention properties, gelling ability, emulsifying properties, and stabilizing properties. Many of these properties depend on the specific chemical nature of the colloid, and because the different agents have different properties, each find specific niche uses. Most of the colloids in current use either give viscous solutions, strong gels, or have chemical functional groups which specifically interact with other materials. While this may be useful for certain applications, it can be a disadvantage on other occasions.

The materials described in this invention is a neutral non-interacting colloid with low gel strength and which has properties which are either difficult to obtain with other materials, or which will at least provide the public with a

useful choice. There are a range of products with a narrow range of properties which depend on the origin of the material. Whereas the normal purpose of agars is to give a firm texture in the end result, to suspend materials or to hold them together, in other words the focus is generally on the solid components, the most common use envisaged for these materials is for carrying and releasing fluid, especially water and materials dissolved in it, in other words the focus is generally on the fluid it contains. It is for this reason that the gel is made deliberately weak, namely to make it easy for the controlled release of liquid.

The preferred material for many applications is a polymer with as little substitution as possible, and this type of polymer is best obtained by hydrolysis of an agar of high gel strength under controlled acidic conditions. Acid hydrolysis is a well known method for degrading agar, and generally it has been used to determine the constituent sugar in agar. The essence of this invention is that it is possible to control such a hydrolysis, to prepare new materials suitable for use to which agar itself is far less suitable.

Alternative methods of obtaining the low gel strength polymer are available, however, and include oxidative degradation, fractionation of the polymer and also alkali treatment of the agaropectin molecules. A further method is to heat the moist solid in the presence of certain inorganic materials, which is a variation of the hydrolysis method. The acid hydrolysis is, however, the most readily controlled method of obtaining this material.

The starting material for the preparation of the low gel strength agars of this invention can also be specific seaweeds which produce such low gel strength agars naturally, and without limit to the generality, may include certain **Gracilaria species**, especially those whose gel strength has otherwise been considered too weak to be of commercial interest, including as an example, but

without limit on the generality, Gracilaria secundata which when extracted, even after rigorous alkali treatment, has a gel strength in the order of 35g/cm², and from the Ceramiaceae and Rhodomelaceae, where specific substitution on the agar-type molecule may give properties of specific interest. A specific example is the agar from Euptilota formosissima, which, following alkali treatment and extraction, has a gel strength up to 140g/cm², and has the 6-hydroxyl group of the D-galactose units almost completely methylated, which in turn will give the material more hydrophobic properties. This agar, following short acid hydrolysis, gives a very low gel strength agar with the creamy nature, but the more hydrophobic nature of the agar gives this agar a different texture, and it should also be more useful for dispersing more hydrophobic components, such as oils and some flavours.

The material can also be obtained from seaweeds which would normally produce agar with a high gel strength, but which have undergone biological degradation, for example through storage under damp conditions, or through being left for too long on the beach prior to collection, or also from normal agar manufacture where gel degradation has occurred. Accordingly this product will be expected to be of considerable value in that it permits the use of material which would otherwise be rejected.

The most straightforward hydrolysis technique is to dissolve the agar in boiling water and add an acidic buffer. After a suitable length of time, which depends on the chosen PH of the solution and the initial gel strength of the agar, the solution is made neutral, and for control purposes this neutralization may include the use of a salt, or acid, which has buffering capacity at around pH7, such as phosphate, and the solution is cooled and allowed to gel. One such acid buffer is sodium hydrogen sulphate, which when 0.125% by weight is added, gives a pH in the order of 1.4, and for an agar with a gel strength of 1000g/cm² is reacted at 98 degrees for between 1 minute and

20 minutes, preferably between 5 and 12 minutes, to give a gel with a gel strength of about 60/g/cm² (5 minutes) or 10g/cm² (10 minutes). Certain polyacids such as citric acid, or pyromellitic acid, can act as an acid buffer for the controlled hydrolysis, and also provide buffering to control the neutralization.

The rate of hydrolysis depends on the strength of the acid. Thus when reacting an identical sample under the same conditions as above, at a pH of 2.6, after one hour the gel strength was 40g/cm², while at pH 4.3, after 1hr 30 mins, there was no significant loss of gel strength when compared with the original sample. A sample of wet powdered agar, pH of approximately 4.5, was held at 60 degrees for two days, and a material with a gel strength of approximately 10g/cm² was obtained. These times are given as guides for making the product, however the precise times of reaction will be expected to depend to some extent on the nature of the raw material. The method is applicable to agars with methyl ethers. Thus a 1.5% solution of **Gracilaria** agar which initially had a gel strength of 600g/cm², when made acid at pH 1.4 for five minutes at 100 degreees, then neutralized, gave a gel strength of 30g/cm². Similarly, a 1.5% gel made from the alkali treated agar-like extract from **Euptilota formosissima**, which had a gel strength of 140g/cm², when made acid at pH 1.4 for three minutes at 100 degrees, then neutralized, gave a gel with a strength of 10g/cm²

The rate of hydrolysis also depends on the concentration of the acid, even though the pH is the same. Thus when 26g of agar, gel strength 750g/cm² were dissolved in 1.5 litres of water at 95 degrees C, the addition of 500mg of citric acid, following by adjustment of pH to 3.25, gave a gel with strength 40g/cm² after 25 minutes, and the creamy material with almost zero gel strength after 35 minutes. If, on the other hand, the experiment was repeated with 300mg of citric acid, and the pH adjusted to 3.25, after 35 minutes the gel had a strength of 50g/cm².

The exact gel strength obtained is dependent on the specific conditions, and the nature and purity of the agar, and these gel strengths should be considered as examples obtained from this specific set of conditions. It is the method of the invention to obtain a low gel strength agar from the high gel strength material by heating it with an acid catalyst, and a very wide range of possible conditions can be expected within the scope of this invention. Thus for practical reasons the pH range of between 1 and 3.5 would seen to be the most useful, but extremely rapid flash hydrolysis with stronger acid, the use of weaker acids at elevated temperatures in pressurized reactors, or hydrolysis for far longer times with weaker acid is still within the scope of this invention.

Thus if 200ml if a 1.5% solution of a slightly coloured agar of gel strength 800g/cm^2 is heated at 118 degrees for 2 hr with 0.4g sodium bisulphite, which will have a pH initially below 6, a white agar with a gel strength of about 10g/cm^2 was obtained. The use of pressure will be of particular value if the acid catalyst also functions as a preservative, as in the case the hot solution can be immediately used without further purification, and no isolation of the low gel strength agar is required. Accordingly, all uses of acidic preservatives for the preparation of this low gel strength material are within the scope of this invention.

Once the hot solution is prepared, it should be neutralized, eg. by sodium hydroxide or sodium carbonate, and if desirable, the solution can be subjected to chemical reduction, preferably by adding a small amount of sodium borohydride, to remove colour generated from the hydrolysis. Hydrolysis at elevated temperatures using sodium bisulphite will automatically hydrolyse the material and maintain a white colour to the product.

This solution can be used as is, if the sodium sulphate can be tolerated, the

sodium sulphate can be removed by means generally known to those practiced in the art, eg by ion exchange, dialysis, washing through ultrafiltration, etc, or the low gelling strength agar can be isolated by means generally known to those practiced in the art, eg direct drying, or through prior concentration, eg through ultrafiltration. For all but the weakest gels, a convenient method of concentration is to allow the solution to gel from a reasonably concentrated solution, then to freeze it, then to thaw it and wash/dialyse it in warm water. The agar is readily dialysed, and the solid can be recovered by pouring the solution over a fine mesh and allowing it to drain. Once drained, gentle squeezing will extrude further water. This method has the advantage that it allows easy purification by washing out unwanted salts. However, the method of dewatering the gel can be chosen for convenience, and is not critical to the subject of this invention.

The lower gel strength agar can also be prepared from high gel strength material by oxidation. To the solution of agar, a suitable oxidizing agent or mixture of agents is added. One of the more effective methods is to add a suitable amount of sodium hypochlorite, followed by an equivalent amount of hydrogen peroxide, with rapid stirring. The exact amount of oxidizing agent required is dependent on the impurities present in the agar, and should be determined by laboratory trial first. The purification of the solution will follow the general methods outlined above, except that a material such as sodium bisulphite can be added to remove surplus oxidizing agent as soon as the reaction is complete. In general, this method is inferior from an economic standpoint because the efficiency of the polymer degradation is low, but the method is considered to be within the scope of this invention.

A further purpose of this invention is to provide uses for these low gel strength agars, and these uses are claimed irrespective of the source of the agar. The low gel strength agar, when cooled from solution, gives a weak gel

which can be easily worked to give a paste-like material with unusual consistency and water retention properties. Uses for this material will frequently involve the agar as providing a base material which will carry water, and other materials mixed or dissolved in it.

Thus one novel use for this material is as a base for massage gels. An agar gel obtained by hydrolysis of **Pterocladia** agar with a strength of approximately 40g/cm² is easily worked, and when applied in the course of massage, provides lubrication for a longer period of time than will other gels. We interpret this as being due to the ability of the gel to retain water, and release it slowly thorugh syneresis, although our claim is based on the observed improved performance and not on this explanation. The gel also acts as a carrier for any soluble agent which may give other useful benefits, such as an anti-inflammatory agent, and it will release this more slowly thorugh the course of the massage than would otherwise be the case. It is also possible to add an agent such as a carrageenan to the gel which can be released to give the skin a pleasant rub-out feel following the massage. For a massage gel, the concentration of low gel strength agar should be in the range of 0.5-20% by weight, although the best effects are found in the range of 1-2% by weight. Increasing the concentration of agar increases the stiffness and reduces the overall lubricating power of the gel, but notwithstanding this, increasing the levels of agar up to the 20% range, which would only be practical if the agar is far more hydrolysed than is indicated elsewhere in this patent, are intended to be included in this claim.

A further use for these low gel strength agars is to produce a mixture which will behave in texture a little like a cream. The material can be easily deformed, or poured, and it behaves as if it had some thixatropic properties. This is particularly the case for those agars at the lowest useful end of their gel strength, eg from 1-20 g/cm². It must be emphasised that at these low gel

strengths, the "strength" is as much a resistance to flow, and the measurement depends to quite an extent on the velocity of the plunger. The gel strengths quoted here are intended for guidance, and are not intended to be definitive physical measurements.

These very low gel strength agars are expected to have uses as suspending agents, eg to slow the flow of, say, an ice cream topping. Such a topping can, however, take advantage of the hysteresis effect in agar gelation, in that since the gel does not remelt until about 85 degrees C, depending on the source of agar, a topping could also be usefully applied to a hot desert, without it melting and running away as many other such toppings would do. Such a topping could include any normal flavours, including crushed fruit, juice, chocolate flavours, caramels, syrups, and also, taking advantage of the fact that some agars can retain quite high levels of alcohol, liqueurs. It should be emphasised that this invention is that of the base material, and the additives noted here are intended as examples rather than as defining the limits of the usefulness of the material.

The use of such mixture is, of course, not limited to toppings, nor is it limited to desserts. Any food use where a thickened sauce-carrier might be required and where this low gel strength agar is employed is considered within the scope of this invention, and this can include liqueur fillings, fillings for cakes, chocolates, etc, internal sauces for desserts, mayonnaises, etc.

The major advantage for foods that we see in this invention is that it is possible through this invention to make a material of a cream-like texture, but which is neutral, that is it does not react with other foods. Such reactions with other foods can, of course, be useful in themselves, eg the carrageenan-milk reaction is the basis of instant puddings, but equally there are some times in food preparation where a non-interactive food thickener is

desirable. This is particularly the case when a range of food mixtures is required, as the thickness of the final product will not depend in any dramatic way as to how the product is made (ie, the order of addition, which is important with some other food additives) or the nature of the additives.
A further advantage lies in the fact that the thickening can be obtained with almost no calories, and totally free of any fat. The only components, besides desired additives, are 98.5% water, or thereabouts, and the remainder an agar which is essentially non-nutritional. Use for preparing diet or diabetic food prepartions is clearly indicated.

While describing this invention, reference has been made to a number of subjective terms to describe texture. The descriptions have been given to assist in outlining the nature of the invention, and such terms are to be regarded solely in this light. The purpose of the invention is to provide the low gelling strength agar as a base for various uses, and is not to be defined by whether such descriptive terms could be used by others.

While the methods outlined above have primarily been concerned with naturally occurring agars, a lower gel strength material can also be obtained by chemically modifying the agar through the addition of substituents. One such product commercially available is a modified agarose produced to give gels which melt at lower temperatures, and coincidentally also have low gel strengths. This material is manufactured for the gelling temperature properties, and any such uses for the low gel strength uses as outlined herein are considered to be within the scope of this invention.

Where in the foregoing description reference has been made to specific c mponents or integers of the invention having known equivalents, then such equivalents are herein incorporated as if individually set forth.

Although this invention has been described by way of example and with reference to possible embodiments thereof it is to be understood that modifications or improvements may be made thereto without departing from the scope or spirit of the invention.

Literature Cited: R Armisen & F Galatos "Production, Properties and Usage of Agar "FAO Fisheries Technical Paper 288, Chapter 1. FAO, Rome, 1987.

EXAMPLES

When Pterocladia agar is used, the agar had previously been alkali treated, and the sample had a gel strength (1.5% solution) of 750g/cm^2.

1. 26g Pterocladia agar was dissolved in 1.4 litres of water at 96 degrees C. 500mg of citric acid was added and the small pH was adjusted to 3.25 by addition of a few drops of dilute hydrochloric acid. The solution was stood at 96 degrees for twenty-five minutes, then the pH was increased to 7 with sodium carbonate solution, 15mg of sodium borohydride was added, the solution was stirred then poured into containers to gel. The gel was frozen then thawed by immersion in warm water, the agar recovered by pouring the liquid onto a gauze, then the agar was dried. On reconstituting, the gel strength was 40g/cm^2.

2. The procedure of example 1 was followed, except that the solution was stood at 96 degrees for 35 minutes. This hydrolysed agar could also be isolated from freeze/thawing, and the resultant material, after being recovered from the gauze was placed in a fine cloth and further water pressed from it. The resultant cheese-like material was dried, and on reconstitution by dissolving in hot water (1.5% solids) and cooling gave a cream-like material with zero gel strength.

3. To 1.5 litres of water at 95% was added 22g of the hydrolysed agar obtained from example 1, then 5g of lambda carrageenan and 1.2g of commercial bacteriostat. The solution was stirred until dissolution was complete, then the solution was allowed to gel, to give a massage gel base which has good lubrication properties, and when rubbed dry leaves a non-oily smooth feel to the skin.

4. To the hot gel base of example 3, 45g of the extract from St John's Wort is added and stirred in. When cooled, the gel can be used for massage, and at the same time the essential oil is applied.

5. The procedure of example 3 is followed, except that the hydrolysed agar from example 2 is used. On cooling a gel base is obtained with creamy texture which can be rubbed in and rubbed dry, to give an oil-free skin with a "velvety" feel.

6. The procedures from examples 1 and 2 were followed using agar from Gracilaria chilensis, which also started with a gel strength of 700g/cm^2. The final products were similar in gel strength to those quoted in these examples, but the weak gels had a different texture, and tended to release water more quickly when the gel was rubbed than the products from Pterocladia.

7. To the bases of examples 1, 2 and 6 cleansing agents, astringtent agents, etc, can be added to allow that function to be completed without leaving an oily residue. Alternatively, small amounts of menthol can be added to give the effect of cooling lotions. The material is applied to the skin the same way a gel or cream is, but on gentle rubbing, it behaves more like a lotion. Thus if 3% of potassium aluminium sulphate and 0.1% bacteriostat are added to a 1.3% solution of the material from example 1,

and the solution is allowed to cool, a gel is obtained which when rubbed on the skin behaves in a very similar fashion to an astringent lotion. When dried, gel material is not discernible, and no staining or otherwise objectionable residues remain.

8. The procedures of examples 3 and 5 are followed, but the lambda carrageenan is replaced by the extract from **Champia nouvelle-zelandia**. The gel is used for the same purpose, but has the advantage that just prior to rubbing dry, the friction on the skin is much reduced, and the final texture is different. Other sulphated polysaccharides can also be used to replace the carrageenan, each giving slightly different textures and performances.

9. The gel bases can also be used to transport aqueous solutions or emulsions with pharmaceutical or other active ingredients to the skin. Thus a solution was prepared by dissolving 1.3 parts of the material prepared from **Gracilaria chilensis**, according to example 1, 0.3 parts fucoidan, and 0.1 parts bacteriostat in 100 parts water and to this was added 3 parts juniper oil dispersed in a mixture of 3 parts of Tween 20 and 3 parts Tween 80. The resultant gel was effective at removing acne, but when applied and rubbed in left no traces of the material which had been applied.

10. Hydrolysates were prepared following the procedures of examples 1 and 2 for the agar from **Curdiea coriaceae**, which has almost two methyl groups per biose unit. 0.67g of this hydrolysate were dissolved in 50 ml of water containing 0.05g bacteriostate at 118 degrees in a pressure vessel. The resultant weak gels behave in a similar way to other agars, except that they do not redissolve in boiling water, and they have a different texture.

11. 0.67g of hydrolysate from Curdiea coriaceae, as described in example 10, was heated in a pressure vessel at 180 degrees in the presence of 16g water. On cooling a syrup was obtained. To this syrup, 48 ml of ethyl alcohol were added carefully with good stirring, the alcohol having been preheated almost to its boiling point. A weak gel similar to those described above is obtained, except that the fluid being carried is 75% alcohol. The alcohol may have essential oils dissolved in it, and may be used as a cooling gel, or as a non-spilling fuel.

12. To 80g of boiling water was added 1.3g of the material of example 2 and 0.2g of preservative, and the liquid was boiled until dissolution was complete. If desired, a thickener, such as lambda carrageenan could be dissolved into the solution, and then a fruit essence or concentrate was added. The volume was made up to 100 ml, and the whole allowed to cool, to give a fruit flavoured cream-like material with almost no calories.

Where in the foregoing description reference has been made to specific components or integers of the invention having known equivalents, then such equivalents are herein incorporated as if individually set forth.

Although this invention has been described by way of example and with reference to possible embodiments thereof if is to be understood that modifications or improvements mya be made thereto without departing from the scope or spirit of the invention. In particular, since the invention describes a gel for carrying fluids for specific purposes, and where additives known to those familiar with the art are included by way f example, other additives may be used with ut departing from the scope of the inventi n.

CLAIMS

1. A process by which an agar or agarose is hydrolysed or partially depolymerized under controlled conditions such that on neutralization a solution is obtained which on cooling gives a gel with a strength in the range of 15-100 g/cm² if the gel has 1.5% concentration of the resultant hydrolysed agar. For the purposes of this claim, the agar may have up to two methyl substituents per agarobiose unit.

2. A process by which agar or agarose is hydrolysed or partially depolymerized under controlled conditions such that on neutralization a solution is obtained which on cooling gives a gel strength in the range of 0-15 g/cm² if the gel has 1.5% concentration of the resultant hydrolysed agar. For the purposes of this claim, the agar may have up to two methyl substituents per agarobiose unit.

3. A process by which the solution from claim one following neutralization may be reduced with sodium borohydride to give white partially hydrolysed agar with improved stability.

4. A process by which the solutions from claim two following neutralization may be reduced with sodium borohydride to give white partially hydrolysed agar with improved stability.

5. The materials of claims 3 and 4.

6. A gel base for application to skin prepared by redissolving the materials of claims 1 or 3 in hot water and allowing to cool.

7. A gel base for application to skin prepared by redissolving the materials of claims 2 or 4 in hot water and allowing to cool.

8. A gel for skin application prepared by adding lambda carrageenan to the gel bases of claims 6 or 7.

9. A gel for skin application prepared by adding carrageenans to the gel bases of claism 6 or 7.

10. A gel for skin application prepared by adding fucoidan to the gel bases of claims 6 or 7.

11. A gel for skin application prepared by adding sulphated polysaccharides from red seaweeds from the Lomentariaceae, Cryptonemiaceae, or Kallymeniaceae to the gel bases of claims 6 or 7.

12. Massage gels prepared by adding essential oils or pharmaceuticals to the gels of claims 8 to 11.

13. Skin cleansing gels by adding water soluble cleansing agents to the gel bases of claims 6 or 7.

14. Skin nutritive, emmollient or moisturizing gels prepared by adding appropriate agents to the gel bases of claims 6 or 7. These agents may include, but are not limited to, the sulphated polysaccharides in claims 8-11.

15. Astringent skin gels prepared by adding astringent agents to the gel bases of claims 6 or 7.

16. Gels for applying insect repellents to the skin using the gel bases of claims 6 or 7.

17. Gels for applying pharmaceutical products to the skin using the gel bases of claims 6 or 7.

18. Gels containing high levels of alcohols, and alcohol soluble materials, using the materials of claims 1 to 4 where the original agar had high levels of methyl ether substituents.

19. Readily deformable gels or cream-like materials for containing or holding syrups, juices, essences, flavours and related food products in food applications, using the materials of calims 1 to 4.

20. A gel for application to the skin, and the hair and fur of animals, prepared by adding alginates to the gel bases of claims 6 or 7.

AMENDED CLAIMS

[received by the International Bureau on 04 July 1995 (04.07.95); original claims 1-4 amended; remaining claims unchanged (3 pages)]

1. A process by which an agar or agarose which consists essentially of agarobiose units with 0.2 methyl groups per agarobiose unit, is hydrolysed or partially depolymerized under controlled conditions such that on neutralization a solution is obtained which on cooling gives a gel with a strength in the range of 10-100 g/cm² if the gel has 1.5% concentration of the resultant hydrolysed agar, and the resultant product is readily obtainable as a coarse solid following freeze-thawing.

2. A process by which an agar or agarose which consists essentially of agarobiose units with 0.2 methyl groups per agarobiose unit, is hydrolysed or partially depolymerized under controlled conditions such as on neutralization a solution is obtained which on cooling gives a gel strength in the range of 0-10 g/cm² if the gel has 1.5% concentration of the resultant hydrolysed agar, and the resultant product is readily obtainable as a coarse solid following freeze-thawing.

3. A process by which the solutions of partially hydrolysed agar from claim 1 following neutralization may be reduced with sodium borohydride to give a white "agaritol" with improved stability.

4. A process by which the solutions of partially hydrolysed agar from claim 2 following neutralization may be reduced with sodium borohydride to give a white "agaritol" with improved stability.

5. The materials of claims 3 and 4.

6. A gel base for application to skin prepared by redissolving the materials of claims 1 or 3 in hot water and allowing to cool.

7. A gel base for application to skin prepared by redissolving the materials of claims 2 or 4 in hot water and allowing to cool.

8. A gel for skin application prepared by adding lambda carrageenan to the gel bases of claims 6 or 7.

9. A gel for skin application prepared by adding carrageenans to the gel bases of claism 6 or 7.

10. A gel for skin application prepared by adding fucoidan to the gel bases of claims 6 or 7.

11. A gel for skin application prepared by adding sulphated polysaccharides from red seaweeds from the Lomentariaceae, Cryptonemiaceae, or Kallymeniaceae to the gel bases of claims 6 or 7.

12. Massage gels prepared by adding essential oils or pharmaceuticals to the gels of claims 8 to 11.

13. Skin cleansing gels by adding water soluble cleansing agents to the gel bases of claims 6 or 7.

14. Skin nutritive, emmollient or moisturizing gels prepared by adding appropriate agents to the gel bases of claims 6 or 7. These agents

may include, but are not limited to, the sulphated polysaccharide in claims 8-11.

15. Astringent skin gels prepared by adding astringent agents to the gel bases of claims 6 or 7.

16. Gels for applying insect repellents to the skin using the gel bases of claims 6 or 7.

17. Gels for applying pharmaceutical products to the skin using the gel bases of claims 6 or 7.

18. Gels containing high levels of alcohols, and alcohol soluble materials, using the materials of claims 1 to 4 where the original agar had high levels of methyl ether substituents.

19. Readily deformable gels or cream-like materials for containing or holding syrups, juices, essences, flavours and related food products in food applications, using the materials of calims 1 to 4.

20. A gel for application to the skin, and the hair and fur of animals, prepared by adding alginates to the gel bases of claims 6 or 7.

STATEMENT UNDER ARTICLE 19

1. The ammendments to claims 1 and 2 have been made because firstly each claim in the original version (refer pages 15 entitled "CLAIMS") involved two sentences. The second sentence was explanatory to define what the starting agar or agarose was. The concept was discussed more fully in paragraph 2 on page 2 and several other places of the Description of Invention. The second change is to add the aspect of freeze-thawing as a test of whether this is the correct material or not; The freeze-thawing was the method of purification as employed is examples 1 and 2 hence is not new material. The technique was also mentioned in paragraph 1 on page 7 of the description of the invention.

2. The changes to claims 3 and 4 have been made for clarity. The partially hydrolysed agars are in the materials of claims 1 and 2. The reduction with sodium borohydride must, perforce, give a reduced material; the aldoses are converted to additols, hence the change in terminology.

3. The changes to claims 3 & 4 have no implications to the remainder of the application other than that it might be desirable to explain the chemical differences between an aldose and an alditol, or provide a literature reference. The changes to claims 1 and 2 are intended to clarify the scope of the original claims. In the first paragraph on page 2 of the description of the invention we wrote: "These initial

weak gels tend to rupture, and in the limit of weakness flow as a sloppy gel. These materials generally consist of agar molecules which have high levels of anionic substitution, for example, sulphate ester, and the preparation of such materials are not the subject of this invention...". These materials which are not the subject of this invention cannot be purified by freeze-thawing (cf Ina Foods EP 0 570 252 A2), and while this difference is mentioned in several places in our application and the description of the invention, the amendment to the claim is intended to emphasize it.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NZ 94/00057

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08B37/12 A61K7/48 A23L1/0532

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08B A61K A23L A23G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 570 252 (INA FOOD INDUSTRY CO) 18 November 1993 see page 3, line 36 - line 44 see page 5, line 12 - line 24 see page 7, line 52 - line 54 see page 26, line 19 - page 27, line 23 --- -/--	1,2,6-8, 12-15, 18-20

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
30 November 1994	17.01.95.

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Lensen, H

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 92, no. 3, 21 January 1980, Columbus, Ohio, US; abstract no. 20874r, MATSUMOTO HARUMI ET AL. 'Effect of organic acid salt pm the gelatinization of organic acid-agar jelly' page 550 ; see abstract & KASEIGAKU ZASSHI, vol.30, no.7, 1979 pages 613 - 617 ---	1
X	CARBOHYDRATE RESEARCH, vol.13, no.2, 1970, AMSTERDAM pages 247 - 256 KENNETH B. GUISELEY 'The relationship between methoxyl content and gelling temperature of Agarose' see page 253; table V see page 256, paragraph THIRD ---	1
A	US,A,4 507 472 (USHER ET AL.) 26 March 1985 see column 1, line 35 - line 38 -----	3,4

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern... al Application No
PCT/NZ 94/00057

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP-A- 6056625	01-03-94
US-A-4507472	26-03-85	EP-A,B 0195151	24-09-86